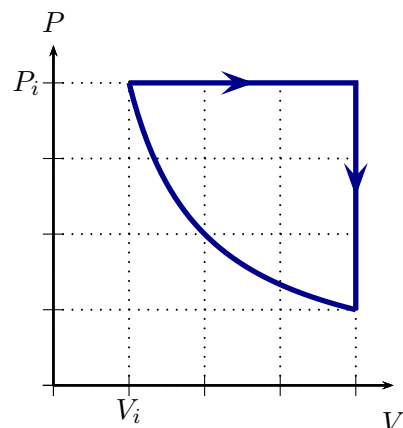


# Statistical and Thermal Physics: Homework 11

Due: 28 February 2020

## 1 Gas interacting with reservoir at constant pressure

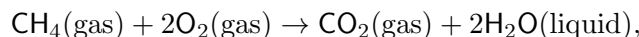
A monoatomic ideal gas interacts with a reservoir, whose temperature is  $T$ . The gas is allowed to expand, interacting only with the reservoir while it does this. Let  $W_{\text{by}}$  be the work done by the gas during this process. The diagram illustrates two processes for the gas. Process 1 is an isothermal expansion at the temperature of the reservoir, represented by the curved line. Process 2 is a constant pressure expansion followed by a constant volume cooling.



- How does the work done by gas in the process 2 compare (larger, smaller, same) to that done by the gas in process 1? Explain your answer.
- How does the change in Helmholtz free energy for process 2 compare (larger, smaller, same) to that for process 1? Explain your answer.
- Is process 2 attainable given that the gas only interacts with the reservoir and its initial and final temperatures are the same as that of the reservoir? Explain your answer.

## 2 Methane combustion

When methane ( $\text{CH}_4$ ) undergoes combustion according to



at 298 K, the change in enthalpy is  $-890 \text{ kJ mol}^{-1}$ . The entropy of the constituents is  $186.3 \text{ JK}^{-1}\text{mol}^{-1}$  ( $\text{CH}_4(\text{gas})$ ),  $205.1 \text{ JK}^{-1}\text{mol}^{-1}$  ( $\text{O}_2(\text{gas})$ ),  $213.74 \text{ JK}^{-1}\text{mol}^{-1}$  ( $\text{CO}_2(\text{gas})$ ) and  $69.91 \text{ JK}^{-1}\text{mol}^{-1}$  ( $\text{H}_2\text{O}(\text{liquid})$ ). Suppose that 1.00 mol of methane undergoes combustion and that this occurs in such a way that the pressure at the beginning and end of the process is the same and that the temperatures are also the same.

- Show that

$$\Delta H = \Delta E + P\Delta V$$

and, assuming that the gases involved are ideal, show that this gives

$$\Delta H = \Delta E + kT\Delta N.$$

Determine the change in energy for the process. *Note that the liquid that results from the reaction no longer plays a role in the gas properties of the system.*

- b) Considering the molecules involved in the reaction as the system, and  $S$  as the total entropy of the system is  $\Delta S \leq 0$ ? Does this suggest that the process is possible or not?
- c) Determine the change in the Gibbs free energy and the maximum work that can be done by the gas in this process. Is this smaller than or larger than the change in energy,  $\Delta E$ , during the process? Provide a physical reason for your answer.
- d) If one generated energy by burning methane, what would be the minimum rate at which methane would have to be burnt (in terms of mols/hour) in order to produce 1.0 kW of power?

### 3 Gibbs free energy

Consider a system that is in contact with a reservoir, which has temperature  $T$  and pressure  $P$ .

- a) Suppose that the system undergoes a process in which it is initially in equilibrium with the reservoir (i.e. has the same temperature and pressure as the reservoir) and is finally in equilibrium with the reservoir. Use the argument involving the first and second law to show that in this process

$$\Delta G - P\Delta V \leq W$$

where  $W$  is the work done on the system and the Gibbs free energy is

$$G = E - TS + PV.$$

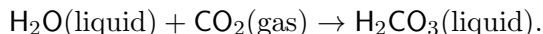
- b) Consider a quasistatic process in which the pressure of the system is constant and equal to that of the reservoir. Assume that no non-mechanical work is done on the system. Show that

$$\Delta G \leq 0.$$

- c) Show that

$$G = H - TS$$

- d) Liquid water and carbon dioxide react as:



For these the enthalpy (of formation from basic constituents) is

$$\Delta H(\text{H}_2\text{O}(\text{liquid})) = -285.83 \text{ kJmol}^{-1}$$

$$\Delta H(\text{CO}_2(\text{gas})) = -393.51 \text{ kJmol}^{-1}$$

$$\Delta H(\text{H}_2\text{CO}_3(\text{liquid})) = -699.65 \text{ kJmol}^{-1}$$

and the entropies are

$$S(\text{H}_2\text{O}(\text{liquid})) = 69.91 \text{ JK}^{-1}\text{mol}^{-1}$$

$$S(\text{CO}_2(\text{gas})) = 213.74 \text{ JK}^{-1}\text{mol}^{-1}$$

$$S(\text{H}_2\text{CO}_3(\text{liquid})) = 187.4 \text{ JK}^{-1}\text{mol}^{-1}$$

Determine  $\Delta G$  for this reaction at 298 K. Will this occur spontaneously without any external non-mechanical work? If not, at what temperature could it occur spontaneously?

a)  $W_{by} = \text{area under } P V \text{ curve}$

The area is larger for process 2  $\Rightarrow$   $W_{by}$  larger for process 2

b)  $\Delta F$  is same since  $\Delta F = F_f - F_i$  and the final points for the processes are same. Likewise initial points are same.

c) In general  $W_{by} \leq -\Delta F$  and the optimal is attained via an isothermal process. This indicates that process 2 is not possible.

More precisely along the constant  $P$  expansion

$$\Delta E = Q + W$$

$\swarrow$   $\searrow$   
 positive negative  
 since temp increases

$$\Rightarrow Q > 0$$

So heat is absorbed. But temp of gas becomes larger than reservoir so it cannot absorb heat from reservoir. Process 2 is impossible

a)  $H = E + PV$

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta(PV) = P_f V_f - P_i V_i$$

$$= P(V_f - V_i) \quad \text{since } P_f = P_i = P$$

$$\Rightarrow \Delta H = \Delta E + P\Delta V$$

For an ideal gas  $V = \frac{NkT}{P} \Rightarrow \Delta V = \Delta N \frac{kT}{P}$

$$\Rightarrow \Delta H = \Delta E + P\Delta V$$

$$= \Delta E + kT\Delta N$$

$$\Rightarrow \Delta E = \Delta H - kT\Delta N$$

Here  $\Delta H = -890 \times 10^3 \text{ J}$

$$\begin{aligned} \Delta N &= \text{change in number of moles of gas} \times N_A \\ &= (-2) \times 6.02 \times 10^{23} \end{aligned}$$

$$\begin{aligned} \Rightarrow kT\Delta N &= -2 \times 1.38 \times 10^{-23} \text{ J/K} \times 298 \text{ K} \times 6.02 \times 10^{23} \\ &= -4.95 \times 10^3 \text{ J} \end{aligned}$$

$$\Rightarrow \Delta E = -890 \times 10^3 \text{ J} + 4.95 \times 10^3 \text{ J} = -885 \times 10^3 \text{ J}$$

b) 
$$\begin{aligned} \Delta S &= S(\text{CO}_2) + 2S(\text{H}_2\text{O}_{\text{liq}}) - S(\text{CH}_4) - 2S(\text{O}_2) \\ &= 213.74 \text{ J/K} + 2 \times 69.91 \text{ J/K} - 186.3 \text{ J/K} - 2 \times 205.1 \text{ J/K} \\ &= -242.9 \text{ J/K} \end{aligned}$$

Yes because both can have large positive  $\Delta S$ .

c)  $G = E - TS + PV$

$$= H - TS$$

$$\Rightarrow \Delta G = \Delta H - T\Delta S$$

and

$$W_{\text{non-mech by}} \leq -\Delta G$$

Then  $\Delta H = -890 \times 10^3 \text{ J}$

all for 1 mol

$$T\Delta S = 298 \text{ K} \left[ S(\text{CO}_2) + S(2\text{H}_2\text{O}) - S(\text{CH}_4) - S(2\text{O}_2) \right]$$

$$= 298 \text{ K} \left[ 213.74 \text{ J K}^{-1} + 2 \times 69.91 \text{ J K}^{-1} \right.$$

$$\left. - 186.3 \text{ J K}^{-1} - 2 \times 205.1 \text{ J K}^{-1} \right]$$

$$= 298 \text{ K} (-242.9 \text{ J K}^{-1}) = -72.4 \times 10^3 \text{ J}$$

$$\Rightarrow \Delta G = -890 \times 10^3 \text{ J} + 72.4 \times 10^3 \text{ J}$$

$$= -818 \times 10^3 \text{ J}$$

smaller than change in  $\Delta E$

So  $W_{\text{non-mech by}} \leq 818 \times 10^3 \text{ J}$

Thus max work is  $818 \times 10^3 \text{ J}$

d) Need  $1000 \text{ W} = 1000 \text{ J/s}$ . So in one hour one needs

$$3600 \times 10^3 \text{ J}$$

Then one mol produces  $818 \times 10^3 \text{ J}$  means we need

$$\frac{3600 \times 10^3 \text{ J}}{818 \times 10^3 \text{ J/mol}} = 4.4 \text{ mol}$$

a)  $\Delta E = W + Q$  for the system.

Now  $\Delta S_{\text{tot}} = \Delta S + \Delta S_{\text{res}} \geq 0$

and  $\Delta S_{\text{res}} = -Q/T_{\text{res}} \Rightarrow \Delta S - Q/T_{\text{res}} \geq 0$

$$\Delta S \geq Q/T_{\text{res}}$$

$$\Rightarrow T_{\text{res}} \Delta S \geq Q$$

Thus  $\Delta E \leq W + T_{\text{res}} \Delta S$

$$\Rightarrow \Delta E - T_{\text{res}} \Delta S \leq W$$

Now if the system is initially + finally at the temperature of the reservoir then  $\Delta(TS) = T_{\text{res}} \Delta S$ , so

$$\Delta E - \Delta(TS) \leq W$$

$$\Rightarrow \Delta(E - TS) \leq W$$

$$\Rightarrow \Delta(G - PV) \leq W$$

$$\Rightarrow \Delta G - \Delta(PV) \leq W$$

But if the initial + final pressures are the same then  $\Delta(PV) = P \Delta V$

$$\Delta G - P \Delta V \leq W$$

b) In this case 
$$W = \int -P dV$$
$$= -P \Delta V$$

So 
$$\Delta G - P \Delta V \leq W \Rightarrow \Delta G - P \Delta V \leq -P \Delta V$$
$$\Rightarrow \Delta G \leq 0$$

c)  $H = E + PV \Rightarrow H - TS = E - TS + PV = G.$

d)  $\Delta G = \Delta H - T \Delta S$

Here 
$$\Delta H = H_{H_2CO_3} - H_{CO_2} - H_{H_2O}$$
$$= -699.65 \text{ kJ/mol} - [-393.51 + 285.83] \text{ kJ/mol}$$
$$= -699.65 \text{ kJ/mol} + 679.34 \text{ kJ/mol}$$

$$\Delta H = -20.31 \text{ kJ/mol}$$

$$\Delta S = S_{H_2CO_3} - [S_{CO_2} + S_{H_2O}]$$
$$= 187.4 \frac{\text{J K}^{-1}}{\text{mol}} - [213.74 + 69.91] \frac{\text{J K}^{-1}}{\text{mol}}$$
$$= 187.4 \frac{\text{J K}^{-1}}{\text{mol}} - 283.65 \frac{\text{J K}^{-1}}{\text{mol}} = -96.25 \frac{\text{J K}^{-1}}{\text{mol}}$$

Thus 
$$\Delta G = \Delta H - T \Delta S = -20.31 \frac{\text{kJ}}{\text{mol}} - 298 \text{ K} (-96.25 \frac{\text{J K}^{-1}}{\text{mol}}) = 8.37 \times 10^3 \frac{\text{J}}{\text{mol}}$$

Since  $\Delta G > 0$  it cannot occur spontaneously without non-mechanical work.  
That requires  $\Delta G \leq W_{\text{non-mech}} \Rightarrow \Delta G \leq 0.$

What temperature?

$$\Delta G = \Delta H - T\Delta S \leq 0$$

$$\Rightarrow \Delta H \leq T\Delta S$$

We have  $\Delta H = -20.31 \text{ kJ/mol}$

$$\Delta S = -96.25 \text{ J K}^{-1}/\text{mol}$$

$$\Rightarrow -20.31 \times 10^3 \text{ J/mol} \leq -96.25 \text{ J K}^{-1}/\text{mol} T$$

$$\Rightarrow T \leq \frac{20.31 \times 10^3 \text{ J/mol}}{96.25 \text{ J K}^{-1}/\text{mol}} \Rightarrow T \leq 211 \text{ K.}$$